

Molecular photon echoes as a signature of vibrational cat states

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Quantum interference between two distinct vibrational trajectories induced by two pulse femtosecond excitation in molecules is shown to result in a photon echo, providing direct evidence of the cat state superposition of Gaussian vibrational wavepackets.
 (OCIS codes: Atomic and molecular physics;(270.0270) Quantum Optics; (020.1670) Coherent optical effects)

Optical femtosecond pulses can be used to control the quantum coherence of the vibrational states in molecules^{1,2}. In particular, a pair of pulses can create the superposition of two distinct coherent states known as cat states³. However, it is usually rather difficult to obtain experimental evidence of nonclassical quantum interference effects from vibrational cat states. In order to overcome this problem, it is useful to study the full nonlinear excitation dynamics in an approximate model suitable to the short time dynamics of the molecule. In this presentation, it is shown that the formation of a vibrational cat state in a molecular transition by a pair of femtosecond pulses at times $t_0 - \tau$ and t_0 gives rise to a photon echo at $t_0 + \tau$. This photon echo is a signature of the quantum interference between two distinct vibrational trajectories in momentum space as shown in figure 1.

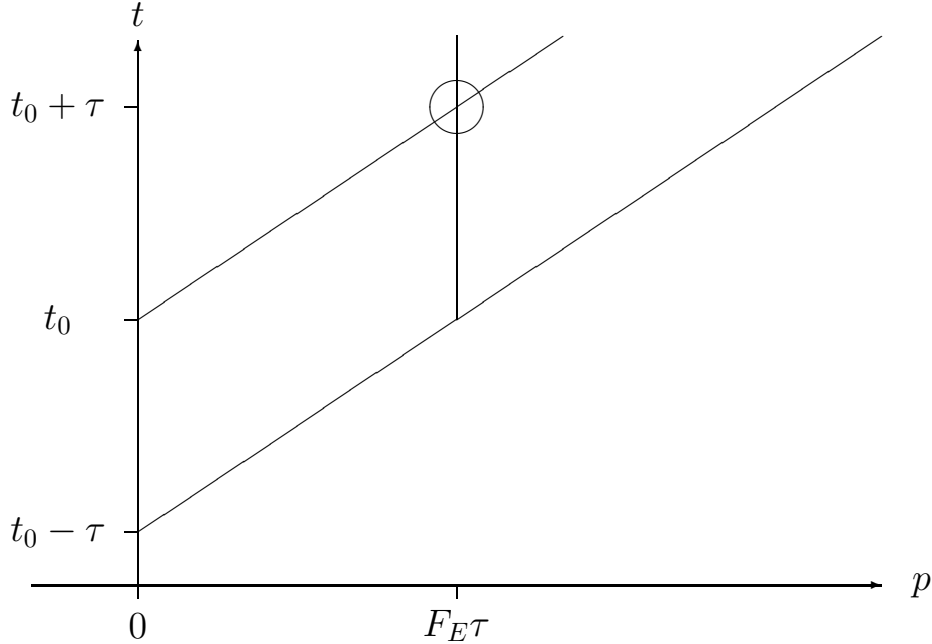


Fig. 1. Time dependence of the vibrational momentum p for femtosecond excitations at $t_0 - \tau$ and t_0 . The excited state is accelerated by a force F_E equal to the slope of the excited state potential. The circle marks the photon echo interference between the ground state and the excited state component at $t_0 + \tau$.

The total vibrational dynamics of a molecule can be described by a Hamiltonian H_0 which reads

$$\hat{H}_0 = \frac{\hat{p}^2}{2m} + V_G(\hat{x}) \otimes |G\rangle\langle G| + V_E(\hat{x}) \otimes |E\rangle\langle E| \quad (1)$$

where the vibrational coordinates are represented by the position operator \hat{x} and the momentum operator \hat{p} , and the electronic system is represented by a ground state $|G\rangle$ and an excited state $|E\rangle$. The projection operators $|G\rangle\langle G|$ and $|E\rangle\langle E|$ select the corresponding vibrational potentials $V_G(\hat{x})$ and $V_E(\hat{x})$. m is the effective mass of the vibration. Initially, the molecule is in the electronic and vibrational ground state, centered around a position $x = 0$ at the minimum of $V_G(\hat{x})$. If the time delay between the two pulses creating the cat state is much shorter than the period of the molecular vibration, it is possible to neglect the vibrational dynamics, approximating the potentials by $V_G(0) = 0$ and $V_E(0) - F_E(0)\hat{x}$. The effective Hamiltonian then reads

$$\hat{H}_0 \approx (V_E(0) - F_E(0)\hat{x}) \otimes |E\rangle\langle E|. \quad (2)$$

This Hamiltonian describes the linear acceleration of the molecular vibration upon excitation. The temporal evolution of an arbitrary initial state may then be given in momentum space by

$$\begin{aligned} \psi_G(p; t) &= \psi_G(p; 0) \\ \psi_E(p; t) &= \psi_E(p - F_E(0)t; 0), \end{aligned} \quad (3)$$

where $\psi_{E/G}(p; t) = \langle E/G; p | \psi(t) \rangle$ is the probability amplitude component of the momentum and excitation eigenstate $|E/G; p\rangle$ of the time dependent quantum state $|\psi(t)\rangle$.

Using this simple evolution to determine the molecular dynamics between a pair of femtosecond pulses, it is a straightforward matter to describe the creation and evolution of a cat state. Initially, the molecular ground state is given by $\psi_G(p; 0) = \psi_0(p)$ and $\psi_E(p; 0) = 0$. At time $t_0 - \tau$, the molecule is excited to $\psi_G(p; t_0 - \tau) = \cos(\phi/2)\psi_0(p)$ and $\psi_E(p; t_0 - \tau) = \sin(\phi/2)\psi_0(p)$. The momentum distribution of the excited state now begins to shift at a rate of $F_E(0)$. At t_0 , a second pulse identical to the first one excites the ground state components and de-excites the excited state components. For $t > t_0$, the state of the molecule is given by

$$\begin{aligned} \psi_G(p; t) &= \cos^2(\phi/2)\psi_0(p) + \sin^2(\phi/2)\psi_0(p - F\tau) \\ \psi_E(p; t) &= \sin(\phi/2)\cos(\phi/2)(\psi_0(p - F(t - t_0)) + \psi_0(p - F\tau - F(t - t_0))). \end{aligned} \quad (4)$$

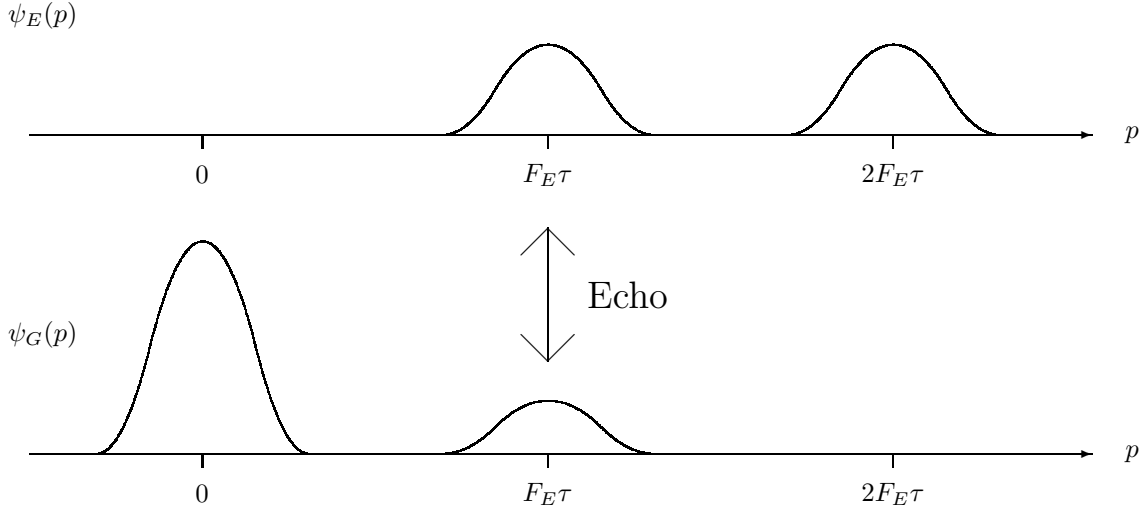


Fig. 2. Schematic illustration of the interference between the vibrational cat states associated with the electronic excited state and the electronic ground state, respectively. The vibrational wavepackets are shown in momentum space at $t_0 + 2\tau$, following a pair of pulses with $\phi = \pi/3$ at t_0 and $t_0 + \tau$.

At $t = t_0 + \tau$, the momentum shift of the last term in $\psi_G(p; t)$ coincides with the momentum shift of the first term in $\psi_E(p; t)$, as shown in figure 2. The quantum coherence between the excited and ground state contributions therefore gives rise to a nonvanishing dipole matrix element. This coherent dipole can be observed as a photon echo.

While the analysis of the quantum dynamics in momentum space clearly reveals that the cause of the photon echo is a cat state coherence between different velocities of the oscillating atoms, the analogy with photon echoes in inhomogeneously broadened spectra suggests an alternative interpretation. Since the approximate Hamiltonian given by equation (2) depends only on the vibrational position \hat{x} and not on the momentum \hat{p} , it is possible to interpret the vibrational quantum state as a probability distribution over vibrational position. The photon echo would then correspond to a rephasing of dipoles associated with well defined atomic positions. This interpretation is entirely sufficient as long as the positional shift induced by the momentum differences is indeed negligible. However, the momentum differences become observable at longer timescales, causing a gradual disappearance of the photon echo. An analysis of the phase space trajectories suggests a decay law of the photon echo intensity I as a function of delay time τ given by

$$\frac{I}{I_0} = \exp\left(-\frac{F^2\Omega}{2\hbar m}\tau^4\right), \quad (5)$$

where Ω is the angular frequency of the molecular vibration. Note that the rather unusual τ^4 dependence should allow a clear distinction between the cat state photon echo in vibrational transitions and the conventional photon echoes in inhomogeneous systems.

In order to satisfy the requirements for the observation of a cat state photon echo, a low frequency of the molecular vibration and a strong electron phonon coupling are necessary. Preliminary studies suggest that an experimental realization of cat state photon echoes is possible using the vibrations of the iodine ion in iodine bridged metal complexes. In this type of molecular system, the approximations applied are valid for time delays τ of about twenty femtoseconds. By applying an experimental setup for photon echo spectroscopy using femtosecond pulses to this molecular system, it should thus be possible to demonstrate cat state interference in molecular vibrations.

One of us (HFH) would like to acknowledge support from the Japanese Society for the Promotion of Science, JSPS.

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